# CEMENT SOLIDIFYING RETARDER AND ITS MANUFACTURE METHOD

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**Invention Title:**

Cement Retarder and Its Manufacture Method

**Abstract:**

A new, high effective cement retarder having super low viscosity for cementing of oil (gas) well and its manufacture method are provided. Highly degraded, refined cotton cellulose, sodium chloroacetate, caustic soda, methanol etc are used as raw material, then neutralized and washed by methanol solution and added hydrochloric acid to obtain methanol-modified carboxymethyl cellulose salt having super low viscosity, namely, the cement retarder of the present invention. Said cement retarder is added to cement slurry and thus obtain various good characteristics, such as good retarding effect, rapid dissolution, low viscosity, good fluidity, temperature resistance, deformation resistance under pressure etc, which meet safe working requirements of cementing of oil (gas) well, especially deep (hot) well.

**Claims:**

1 . A cement retarder (referred as retarder hereafter) used for cementing of oil (gas) well, which uses cellulose as basic backbone and is made of cotton cellulose, caustic soda, hydrochloric acid and water etc, characterized in that highly degraded, refined cotton cellulose is used as raw material, sodium chloroacetate as etherifying agent, the resulting carboxymethyl cellulose salt having super low viscosity (initial product of said retarder) should be neutralized and washed by methanol solution along with added hydrochloric acid, and said retarder must contain methanol.

2. The retarder according to claim 1, characterized by following ranges of formulation (based on the refined cotton cellulose):

| | |
|---|---|
| Refined cotton cellulose | 1 part (by weight) |
| Caustic soda | 0.5-0.7 part (by weight) |
| Sodium chloroacetate | 0.87-1.07 parts (by weight) |
| Water | 2.2-3.1 parts (by weight) |
| Methanol | 0.77-1.37 parts (by weight) |
| Hydrochloric acid | 0.4-0.3 part (by weight) . |

3. The retarder according to claim 1 or claim 2, characterized in that processing conditions of the method of the present invention are:
(1) Alkalization temperature for spaying alkaline process is 30-35□, time period is 1.5-2 hour, concentration of the caustic soda is 20-22%,
(2) Temperature for etherification of basic cellulose by sodium chloroacetate is 30-40□ during the first 30 minutes, and 40-60□ during last 60 minutes,
(3) Time period for washing initial product by methanol solution and hydrochloric acid is 1-1.5 hours, and concentration of methanol is 70-80%.

4. The retarder according to claim 1 or claim 2, characterized in that said highly degradation is mean that degree of polymerization for refined cotton cellulose is less than 400.

**Description:**

The present invention relates to a new, high effective cement retarder (referred as retarder hereafter) having super low viscosity for cementing of oil (gas) well, especially deep (hot) well.

The time for solidification of the cement slurry useful for oil wells not only depends on the chemical and physical performance of cement itself, but also is closely related with the environment (temperature and pressure etc.) in which the cement is solidified as well as additives for cement slurry. Among these, a cement retarder as an additive appears to be particularly important for worker in working place to adjust solidification performance of cement slurry.

Well known and commonly used cement retarders used for cementing of oil (gas) well are tannic acid, ferric chromic salt, tartaric acid, sulfonated tannin and hydroxyethyl saponin gum and so on. In the past years, working temperature of cement slurry is increased significantly (often above 100□) with yearly increase in depth of well being drilled and continue elevation in stratum temperature (circulating temperature of slurry). Therefore, the above-described cement retarders can not meet new requirements any more. Among them, for example, tartaric acid has so strong sensitivity that an increase of 0.01% in the added amount will result in dramatic change of time for solidification of cement slurry. And the added amount less than 0.1% even causes accelerating solidification. Meanwhile, the addition of the additive has shortcoming of extracting water largely. And unsuitably-controlled addition of additive is prone to result in failure of working of cementing well. Tannic acid and ferric chromic salt have good retarding effect on cement slurry at 75□. However, both have bad effect at elevated temperature and generally only suitable for the temperature range of less than 80□. Moreover, the much more foam of ferric chromic salt will destroy the quality of well cementing. Hydroxyethyl saponin gum has good temperature resistance and retarding performance, however, high viscosity of its solution (the viscosity for 2% solution is 82.5 centipoises) will affect the fluidity of cement slurry, and often can not be used alone. Ordinary carboxymethyl cellulose can retard the solidification of cement slurry; however it was only reported in a few documents in China and other countries. It has no practical value and is not

suitable to be popularized due to its high viscosity (the viscosity for 2% solution is 100-250 centipoises), which result in significant deterioration in fluidity of cement slurry. (See, <The experimental study report of CD-CMC cement retarder of super low viscidity>, from Eastern Sichuan Petroleum Drilling Company, Sichuan province, China, 1983).

An object of the present invention is to provide a new cement retarder and the method to produce the same. The cement retarder produced by the method can be used as additive for cement slurry to make cement have good fluidity, good retarding property and strong stability to resist temperature, which can meet working requirements of cementing of oil (gas) well, especially deep (hot) well.

The solution of the present invention is that cotton cellulose is used as basic backbone, and a special method is used to make highly degraded methanol-containing carboxymethyl cellulose salt having super low viscosity, namely, the new, high effective cement retarder having super low viscosity according to the present invention. The special preparation procedure is described as follows.

I. Raw material formulations used in the present invention and requirement:

1. Refined cotton cellulose: water content is 6-10%, the degree of polymerization is less than 400, the amount used is 1 part (by weight), and used as basis for calculation;
2. Caustic soda: concentration is 20-22%, the amount used is 0.5-0.7 part (by weight);
3. Sodium chloroacetate: the amount used is 0.87-1.07 part (by weight);
4. Water: the amount used is 2.2-3.1 parts (by weight);
5. Methanol: concentration is less than 75%, the amount used is 0.77-1.37 parts (by weight);
6. Hydrochloric acid: concentration is 31-36%, the amount used is 0.4-0.8 part (by weight).

II. The preparation procedure of the present invention:

1. Refined cotton cellulose is alkalized by spaying alkaline process with caustic soda, to produce alkaline cellulose, with alkalization temperature being 30-35□, time period 1.5-2 hours.

2. The alkaline cellulose is etherified by sodium chloroacetate to produce carboxymethyl cellulose salt having super low viscosity, that is, initial product of the retarder of the present invention. Etherification time is 1.5-2 hours, and temperature is 30-40□ during the first 30 minutes, and 40-60□ during last 60 minutes.

3. The initial product is neutralized and washed by methanol solution and added hydrochloric acid. Time for washing is 1-1.5 hours, and temperature for washing is room temperature.

4. The washed product is centrifuged, dried, crushed to obtain eligible product, that is, cement retarder having super low viscosity of the present invention.

The carboxymethyl cellulose salt having super low viscosity (containing methanol) produced in the present invention has solubility of less than 6 minutes, viscidity of less than 5 centipoises, and pH of 6-7. Its initial solidification time can be more than 6 hours under various temperature and pressure. The reasons for above properties is that highly degraded cellulose has significantly reduced molecular weight, which make molecular colloid adhere to surface of cement particle to form stronger hydration (protective colloid effect), retarding significantly the time for solidification of cement slurry. The shortcomings that moderately viscous retardant building slurry has big glutinousness and bad fluidity etc are overcome due to low viscidity of carboxymethyl cellulose salt produced in the present invention. Many tests and uses have demonstrated that the retarding performance of the retarder of the present invention is good with the change of the added amount. The resisted temperature may be more than 130□, and the pressure may be up to 4.5 atmospheric pressures. Its use in shallow, moderately deep or deep (hot) well can provide reliable assurance to safe working. Further, the method, raw materials and equipments used in the present invention are all those used in common production in chemical industry. Compared with well-known retarders described above, the retarder according to the present invention has some advantages such as low cost, less amount used, thereby significantly

reducing drilling cost.

Example of the present invention:

100g refined cotton cellulose having 6-10% water content and degree of polymerization less than 400, is alkalized by spaying alkaline process with 270g caustic soda having concentration of 22% at alkalization temperature of 30□ for 2 hours. Resulting alkaline cellulose is etherified by 105g sodium chloroacetate to produce carboxymethyl cellulose salt having super low viscosity, that is, initial product of the retarder. The initial product is then neutralized and washed by methanol solution with concentration of 75% and an amount five times initial product by weight, and added hydrochloric acid, to contain methanol. At last, the washed product is centrifuged, dried, and crushed to obtain purely white flocculent cellulose substance, that is, the cement retarder having super low viscosity of the present invention. The resulting cement retarder is used in cement slurry of oil-producing well in Leshan, Sichuan province, China. When the ratio of water to ash is 50%, and the retarder is added in an amount of 0.1%, 0.2% and 0.3% in water, test temperature is 120□, the initial solidification time is 5 hours and 32 minutes, 6 hours and 28 minutes, 7 hours and 18 minutes respectively, and the viscidity is all less than 4 centipoises, pH is 6-7, and fluidity is all 26 cm.

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〔54〕发明名称 水泥缓凝剂及制造方法

〔57〕摘要

一种油(气)井固井用的新型高效超低粘度水泥缓凝剂及制造方法，以高度降解的精制棉纤维素、氯乙酸钠、烧碱、甲醇等为原料，并经甲醇液加盐酸中和洗涤，制成含甲醇改性的超低粘度羧甲基纤维素盐即本发明缓凝剂。用它加入水泥浆中，具有缓凝效果好、溶解快、粘度低、流动性好、抗温、受压不反常等特点，能够满足油(气)井，特别是深(热)井固井安全施工的要求。

# 权 利 要 求 书

1. 一种油（气）井固井用水泥缓凝剂（以下简称缓凝剂），以纤维素为基本骨架，由棉纤维素、烧碱、氯乙酸及水等制成，其特征在于采用高度降解的精制棉纤维素作主要原料，以氯乙酸钠作醚化剂，所得超低粘度羧甲基纤维素盐（即缓凝剂初制品）应经甲醇液加盐酸中和洗涤处理，本缓凝剂必须含甲醇。

2. 根据权利要求1所述的缓凝剂，其特征在于其配方范围是：（以精制棉纤维素作基准计）

| | |
|---|---|
| 精制棉纤维素 | 1份（重量） |
| 烧碱 | 0.5—0.7份（重量） |
| 氯乙酸钠 | 0.87~1.07份（重量） |
| 水 | 2.2～3.1份（重量） |
| 甲醇 | 0.77~1.37份（重量） |
| 盐酸 | 0.4～0.8份（重量） |

3. 根据权利要求1或2所述的缓凝剂，其特征在于本发明方法的工艺条件是：

(1) 喷碱法碱化温度为30～35°C，时间1.5～2小时，烧碱浓度为20～22%.

(2) 氯乙酸钠醚化碱纤维素的温度为前30分钟30～40°C，后60分钟40～60°C.

(3) 甲醇液加盐酸洗涤初制品时间为1—1.5小时，甲醇浓度70～80%.

4. 根据权利要求1或2所述的缓凝剂，其特征在于所指高度降解是指精制棉纤维素的聚合度应小于400.

# 说　　明　　书

## 水泥缓凝剂及制造方法

本发明属于一种油（气）井，特别是深（热）井中固井用的新型高效超低粘度水泥缓凝剂（以下简称缓凝剂）。

油井水泥浆的凝结时间长短，不仅由水泥本身的化学和物理性能决定，还与水泥浆凝结的环境（温度、压力等）以及水泥浆添加剂都有着密切的关系，而诸因素中，作为添加剂的水泥缓凝剂对于现场施工人员调节水泥浆凝结性能尤其显得重要。

公知的常用油（气）井固井用水泥缓凝剂有：单宁酸、铁铬盐、酒石酸、磺化单宁及龙胶粉等。近年来，随着钻井深度逐年增加，地层温度（泥浆循环温度）不断增高，水泥浆的使用温度也明显增高（经常在100°C以上）。因此，上述缓凝剂已不能适应需要，其中酒石酸敏感性太强，添加量增加万分之一，水泥浆的凝固时间便会急剧变化，而添加量在0.1%以下时，甚至会出现催凝现象，同时加入添加剂还有析水大的缺点，掌握不好易造成固井施工失效；单宁酸与铁铬盐对75°C水泥浆有较好的缓凝效果，但在高温环境下效果差，一般只适用于80°C范围内，而且铁铬盐泡子多，影响固井质量；龙胶粉有较强的抗温及缓凝性能，但溶液粘度高（2%溶液的粘度825厘泊），影响水泥浆的流动性，往往不能单独使用，一般的羧甲基纤维素对水泥浆有缓凝作用，但这只在国内外资料上有过报导，由于粘度高（2%溶液100～250厘泊），致使水泥浆流动性显著变差，因而

无实用意义，更不宜推广。（见1983年四川省石油局川东石油钻探公司的《CD—CMC超低粘度水泥缓凝剂试验研究报告》）。

本发明的目的在于提供一种新的水泥浆缓凝剂及制造方法，使该方法生产的缓凝剂作为水泥浆添加剂，能使水泥浆有好的流动性，缓凝性及较强的抗温稳定性，能满足油（气）井，特别是深（热）井固井施工的需要。

本发明的解决方案是以棉纤维素为基本骨架，以特殊方法制成高度降解的含甲醇的超低粘度的羧甲基纤维素盐，即本发明所指的新型高效超低粘度水泥缓凝剂。其具体作法如下：

一、本发明所用原料配方及要求：

1.精制棉纤维素：含水量6～10%，聚合度不大于400，其用量1份（重量），并以此作为计算基准。

2.烧碱：浓度20～22%，用量0.5～0.7份（重量）。

3.氯乙酸钠：用量0.87～1.07份（重量）。

4.水：用量2.2～3.1份（重量）。

5.甲醇：浓度75%以下，用量0.77～1.37份（重量）。

6.盐酸：浓度31～36%用量0.4～0.8份（重量）。

二、本发明制造过程：

1.用烧碱将精制棉纤维素进行喷碱法碱化，生成碱纤维素，碱化温度30～35°C，时间1.5到2小时。

2.用氯乙酸钠醚化碱纤维素，生成超低粘度羧甲基纤维素盐，即本发明缓凝剂初制品。醚化时间为1.5—2小时，温度为前30分钟30～40°C，后60分钟40～60°C。

3.用甲醇液加盐酸中和洗涤初制品，洗涤时间为1～1.5小时，温度为室温。

4.将洗涤后的产品经离心，干燥粉碎后得到合格品，即超低粘度水泥缓凝剂。

本发明制取的超低粘度羧甲基纤维素盐（含甲醇）其溶解性小于6分钟，粘度小于5厘泊，PH值6—7，初凝时间在不同环境温度和压力下均可达到6小时以上。这是由于经高度降解后的分子量大大减少，使分子胶体吸附于水泥颗粒表面形成较强的水化（护胶作用），明显地延缓水泥浆的凝结时间；由于本身粘度低，克服了中粘缓凝剂配浆粘滞性大、流动性差等问题，经多次试验和使用，证明本发明缓凝剂随加量变化缓凝线性好，抗温可达130°C以上，受压可达4.5个大气压不反常，无论在浅、中深井或深（热）井中使用均能给施工安全提供可靠保证。再有，本发明所采用的方法，原料及设备均为常规化工生产使用，较前述公知缓凝剂，本缓凝剂有成本低、用量少等优点。因此，也大大降低了钻井成本。

本发明实施例：

取含水量6～10%，聚合度小于400的精制棉纤维素100克，用浓度22%的烧碱270克对其进行喷碱法碱化，碱化温度30°C，时间2小时，

所得碱纤维素再用105克氯乙酸钠进行醚化，生成超低粘度羧甲基纤维素盐，即缓凝剂初制品，然后用浓度75%重量为初制品五倍的甲醇溶液加盐酸进行中和洗涤使其含甲醇，最后经离心、干燥、粉碎后得到纯白色絮状纤维物质，即本发明超低粘度水泥缓凝剂，用于四川省乐山产油井水泥浆，当水灰比为50%，缓凝剂添加量为水中含量的0.1%、0.2%、0.3%，试验温度120°C时，其初凝时间分别为5小时32分、6小时28分和7小时18分，粘度均小于4厘泊，PH值为6—7，流动度均为26厘米。